

wave frequency but peak separation is constant and independent of frequency. Saturation of the electrode surface is evident at long adsorption accumulation times, Fig.2, as it was for differential pulse AdSV [3].

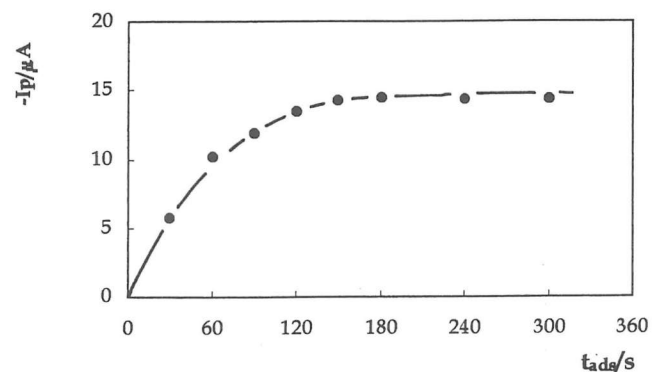


Fig.2 SWAdSV of cobalt: variation of peak current for reduction of adsorbed cobalt-nioxime complex with adsorption time, t_{ads} ; $[Co^{2+}] = 8nM$. Square wave parameters: amplitude 30mV, frequency 100Hz, scan increment 2mV.

Calibration curves have slopes of $0.7\mu A/nM$ for nickel and $1.3\mu A/nM$ for cobalt under optimised experimental conditions (compare $0.08\mu A/nM$ and $0.17\mu A/nM$ for DPAdSV [3]), which represents a sensitivity enhancement of an order of magnitude.

Final remarks

Square wave anodic and adsorptive stripping voltammetry at wall-jet mercury thin-film electrodes is shown to be successful and leads to the same nanomolar detection limits and similar sensitivities as compared to the differential pulse analogues. The particular advantages arise from the removal of the necessity for solution deoxygenation and the faster determination step which can usefully increase sample throughput. This is of importance in on-line monitoring applications.

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ELECTROCHEMICAL REDUCTION OF FLUOXETINE

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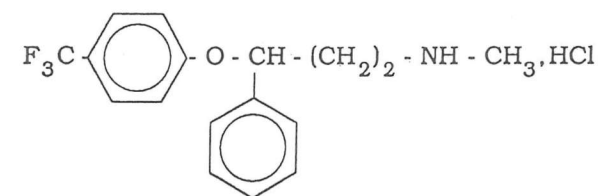
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ABSTRACT

The electrochemical reduction of fluoxetine was studied using a hanging mercury drop electrode in different buffer solutions up to pH 13 and with concentrations of fluoxetine varying from $1.0 \times 10^{-6} M$ to $5.0 \times 10^{-5} M$. A very strong adsorption of fluoxetine on the electrode was observed and the shape of the cyclic voltammograms suggests that in these conditions it corresponds to a quasi-reversible system for adsorbed species. The results obtained for the electrochemical quantification of fluoxetine in five pharmacological formulations existing in the Portuguese market were compared.

INTRODUCTION

Fluoxetine is an anti-depressive used very successfully due to its small secondary effects, namely cardiovascular and colinergic. Its action is through inhibition of the uptake of serotonin by the neurons in the brain, consequently enhancing serotonin neurotransmission.



Fluoxetine is clinically administered in the form of chlorhydrate. It has been also used in the treatment of depression associated with desintoxication of cocaine [1], alcoholism [2], etc., and corresponds to N-methyl-3-[4-(trifluoromethyl) phenoxy] benzenepropanamine.

EXPERIMENTAL

Chemicals and solutions

Fluoxetine chlorhydrate was kindly supplied by Eli Lilly Pharmaceuticals (Indianapolis, IN, USA). All experiments were performed in 0.1M Ringer buffer, and were prepared using purified water from a Millipore Milli-Q system.

Apparatus and procedures

The working electrode was a hanging mercury dropping electrode (HMDE), the counter electrode a glassy carbon rod, and the reference electrode was a AgCl/Ag/KCl 3M, which were used in a one-compartment fluoxetine cell. Voltammograms were recorded using a μ Autolab potentiostat/galvanostat running with model GPES version 3 software, from Eco-Chemie, Netherlands. The potential range studied was from -0.8 V to -1.60 V vs. AgCl/Ag, cyclic voltammetry scan rates varying from 20 to 800 mV s⁻¹

RESULTS AND DISCUSSION

The electrochemical reduction of fluoxetine was studied using a hanging mercury drop electrode (HMDE) in different buffer solutions up to pH 13 and with concentrations of fluoxetine varying from 1.0x10⁻⁶M to 5.0x10⁻⁵ M.

A very strong adsorption of fluoxetine on the electrode surface was observed. The voltammetric curve, Fig.1, shows results obtained at pH 12.1. The shape of the cyclic voltammograms suggests that in the conditions used it corresponds to a quasi-reversible system for adsorbed species since there is very little separation between anodic

and cathodic peaks, the curve is almost symmetric round E_p and the peak current is proportional to v .

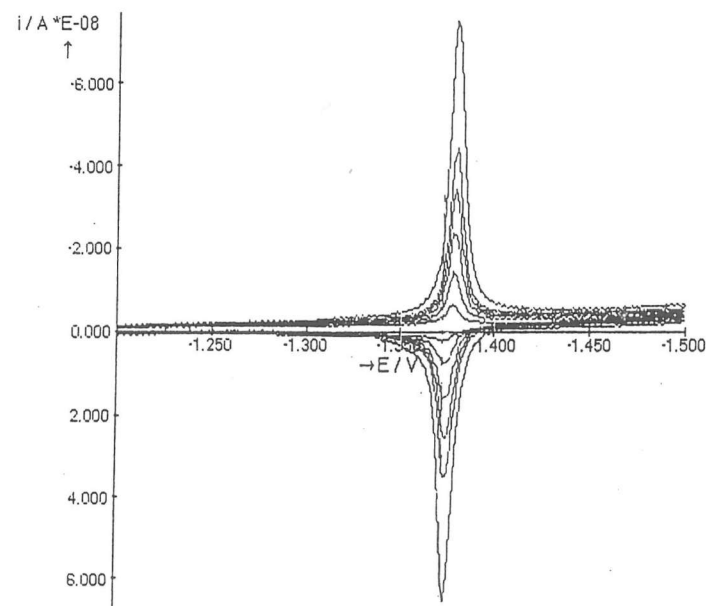


Fig.1 Cyclic voltammograms of 2.38×10^{-5} M fluoxetine in 0.1M Ringer-buffer solution pH = 12.1. Scan rates: 20, 40, 60, 80, 100, 150 mV s⁻¹.

In fact, for analytical purposes linear scan adsorptive stripping voltammetry was used at a scan rate of 800 mV s⁻¹ from -0.8V to -1.6V, preceded by accumulation of fluoxetine on the electrode surface during 10s at 500 r.p.m. stirring rate followed by 10s without stirring, at a potential of -0.8 V.

In the presence of acetonitrile the symmetry of the peak improves and, although there is a small shift in the peak potential to more negative values, since the resolution is better it is possible to determine lower concentrations of fluoxetine in the range 3.2x10⁻⁷M to 2.8x10⁻⁶ M.

The analyse of fluoxetine in five pharmacological formulations, all in the form of chlorhydrate and to be administered orally as capsules, was performed in a 0.05 M Ringer buffer pH 12.1 with 20% acetonitrile, using the standard addition method.

Results obtained for the electrochemical quantification in five different pharmaceutical formulations existing in the Portuguese market are presented in Table 1.

Tabel 1. Pharmaceutical formulations containing fluoxetine*

Name	Laboratory	Fluoxetine(mg/cap)	N° of samples
Prozac	El Lilly	21.58 ± 3.82	4
Prozac	El Lilly	19.15 ± 2.50	4
Prozac	El Lilly	19.80 ± 1.08	4
Prozac	El Lilly	20.39 ± 0.69	3
Tuneluz	Baldacci	18.58 ± 1.35	2
Psipax	Laborterapia S.A.	21.83 ± 0.58	2
Digassim	Vitória	19.96 ± 1.16	2
Nodepe	Eurolabor	20.37 ± 1.83	3

* All formulations refer to 20 mg of Fluoxetine per capsule.

CONCLUSIONS

The electroanalytical method is convenient for the study of the reduction mechanism of fluoxetine. It can be used for its quantification in commonly used pharmaceutical drugs and for the determination of therapeutic doses in biological fluids when coupling high performance liquid chromatography (HPLC) with electrochemical detection.

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THIOUREA DEGRADATION AND ITS CONTROL

-AN ELECTROCHEMICAL STUDY

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Abstract

Thiourea is a promising non-cyanide lixiviant for gold hydrometallurgy. However, its high consumption due to degradation has hindered thiourea from commercial application. Thiourea oxidation is discussed and the role of sodium sulphite as a reductant in controlling the degradation of thiourea is investigated.

Key Words: Thiourea; degradation; noble metals; gold; cyclic voltammetry

Introduction

Thiourea $(\text{NH}_2)_2\text{C}=\text{S}$ is considered as one of the most promising non-cyanide reagents for gold ores leaching[1-4]. Despite high rates of metal extraction, insensitivity to impurity interferences and non-toxicity [4-10], the commercial adoption of the process has been hindered by excessive consumption, due to chemical degradation thiourea via formamidine disulphide (RSSR) (where $\text{R}=(\text{NH}_2)(\text{NH})\text{C}$) and subsequent elemental sulphur formation:



Gold leaching by thiourea is usually conducted in acidic ferric solutions which have potentials higher than that of reaction (1), giving rise to a fast reduction to formamidine disulphide. The case of more moderate oxidants, such as H_2O_2 , can reduce the consumption of the lixiviant but is not economically attractive (lower gold dissolution rates and higher reagent costs).